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A molecularly based theory for electron transfer reorganization energy

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Using field-theoretic techniques, we develop a molecularly based dipolar self-consistent-field theory (DSCFT) for charge solvation in pure solvents under equilibrium and nonequilibrium conditions and apply it to the reorganization energy of electron transfer reactions. The DSCFT uses a set of molecular parameters, such as the solvent molecule's permanent dipole moment and polarizability, thus avoiding approximations that are inherent in treating the solvent as a linear dielectric medium. A simple, analytical expression for the free energy is obtained in terms of the equilibrium and nonequilibrium electrostatic potential profiles and electric susceptibilities, which are obtained by solving a set of self-consistent equations. With no adjustable parameters, the DSCFT predicts activation energies and reorganization energies in good agreement with previous experiments and calculations for the electron transfer between metallic ions. Because the DSCFT is able to describe the properties of the solvent in the immediate vicinity of the charges, it is unnecessary to distinguish between the inner-sphere and outer-sphere solvent molecules in the calculation of the reorganization energy as in previous work. Furthermore, examining the nonequilibrium free energy surfaces of electron transfer, we find that the nonequilibrium free energy is well approximated by a double parabola for self-exchange reactions, but the curvature of the nonequilibrium free energy surface depends on the charges of the electron-transferring species, contrary to the prediction by the linear dielectric theory. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4936586]

I. INTRODUCTION

Electron transfer (ET) is a ubiquitous mechanism in many chemical, electrochemical, and biological processes. The ET kinetics depends on the nonequilibrium free energy surfaces of the reactant and the product states generated by the electron-transferring species and the solvent degrees of freedom.[1–6] The celebrated Marcus theory[7,8] envisions the nonequilibrium free energy surface as two equal-curvature parabolic functions of a one-dimensional macroscopic coordinate — the solvent orientational polarization, based on a linear dielectric treatment of the solvent in terms of its static and optical dielectric constants. This simple picture has had wide successes in many experimental and simulation tests. In particular, the prediction — and subsequent experimental observation — of an inverted region in the energy gap law[5] represents a great triumph of the Marcus theory.

The treatment of the solvent as a linear dielectric medium is clearly an approximation, as recognized by Marcus himself and others.[9–11] Two notable discrepancies have been known in the literature. First, computer simulations indicated that the solvent reorganization energy depends on the charges of the donor-acceptor system,[12–18] not only on the amount of charge transfer as predicted by the Marcus theory. Second, time-resolved spectroscopic measurements of electron-transferring species revealed differences in the energies and shapes of the absorption and the emission bands, while the Marcus picture predicts a perfect symmetry between the two bands.[11,19,20] The explanation of these phenomena requires theoretical methods that account for solvent properties beyond the linear dielectric approximation, such as spatially varying dielectric response and dielectric saturation.

Molecular dynamics (MD) simulations with explicit solvents can include the microscopic molecular structure and interactions, allowing dynamical details of ET processes to be studied.[17,18,21–30] However, multiple long trajectories are required to perform umbrella sampling, making it impractical to perform calculations for general solvents. Integral-equation theories[31–38] are a more convenient alternative to the laborious nonequilibrium sampling schemes in MD simulations, but nanosecond MD simulations are still required to compute the solvent correlation functions in these approaches. Also, it is cumbersome to include the induced dipoles of the solvent in simulations and integral-equation theories; as such, these methods often treat solvent molecules as nonpolarizable, with the effects of solvent electronic response approximated or ignored. Furthermore, these methods require specific, well-parameterized solvent models.

On the other hand, phenomenological treatments[11,39–56] are convenient tools that elucidate the essential physics in electron transfer reactions and provide good explanations for experimental and simulation data by invoking *ad hoc* fitting parameters. However, for any specific ET system, to make *a priori* predictions of the reorganization energy, it is desirable to develop a theory that captures the most important properties of each solvent using only readily available parameters from physicochemical handbooks.

Recently, Nakamura *et al.*[57] developed a coarse-grained theory for equilibrium ion solvation in liquids and liquid mixtures using field-theoretic techniques. The term

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"coarse-grained" refers to a simplified description of the solvent molecules using a reduced set of degrees of freedom. The theory accounts for the molecular nature of the solvents by using a small number of molecular parameters that are readily available — the permanent dipole, the polarizability, and the molecular volume for the solvent and the ionic radius for the ionic solute. The theory naturally captures spatially varying dielectric responses and dielectric saturation in the close vicinity of the ion. With no adjustable parameters, the theory predicts solvation energies in both single-component liquids and binary liquid mixtures that are in excellent agreement with experimental data. A key insight of the work in Ref. 57 is that the solvation energy of an ion is largely determined by the local response of the permanent and induced dipoles, as well as the local solvent composition in the case of mixtures, and bears no strong correlation with the *bulk* dielectric constant.

In this article, we extend the work of Nakamura *et al.* to the calculation of nonequilibrium solvation energy (the reorganization energy) for electron transfer reactions in simple molecular liquids. In contrast to equilibrium ion solvation where both the electronic and orientational components of the solvent polarization reach full equilibrium, the nonequilibrium solvation energy in ET involves conditions where only the electronic polarization responds to the instantaneous solute charges while the orientational component is kept at nonequilibrium values because of the longer time scales for solvent orientational relaxation compared to the electronic motion. The field theoretical formulation naturally accounts for these two different degrees of freedom by introducing two respective conjugate fields (which become identical under full equilibrium conditions). With the same set of molecular input as for equilibrium solvation, and with no adjustable parameters, our theory predicts reorganization energies for a variety of charge transfer reactions involving simple metal ions in good agreement with experimentally obtained data. Furthermore, by treating all solvent molecules on equal footing and representing the solvent polarization as spatially varying quantities, our theory provides a unified description of the solvation energy contributions from all the solvent molecules, thus avoiding the need to separately treat the inner-sphere and the outer-sphere molecules, as is commonly done in existing ET theories. Our approach allows ET reorganization energy to be calculated with minimal computational effort, typically less than half a minute on a personal computer.

The rest of this article is organized as follows. In Section II, after a brief description of the setup of the problem to identify the relevant energies, we formulate our dipolar self-consistent-field theory (DSCFT) for charge solvation under both equilibrium and nonequilibrium conditions for a single-component liquid. (Extension to liquid mixtures will be deferred to a forthcoming paper.) The key equations and main steps in the derivation are presented, while some of the technical details are delegated to the two appendices. In Section III, we present the results for the reorganization and activation energies for several prototypical ET reactions. We show that the DSCFT is able to unify the treatment of inner-sphere and outer-sphere solvent molecules to provide a reliable estimate of the total reorganization energy. In addition, we show that the nonequilibrium free energy surface is well described by a parabolic function, but contrary to the prediction by the linear dielectric theory, the curvature of the free energy surface is not independent of the magnitude of charge on the electron-transferring species. Finally, in Section IV, we summarize the main points of this work and offer some concluding remarks.

II. DSCFT

In this section, we derive the DSCFT by extending the equilibrium theory for ion solvation by Nakamura *et al.* to the case of nonequilibrium solvation with arbitrary solute charge distribution. We start with a brief review of the key concepts in ET theory to define the relevant free energies. Next, we formulate the field-theoretic DSCFT theory for the solvation of a solute with arbitrary charge under equilibrium and nonequilibrium conditions. We then apply the DSCFT to ET between two simple ions, detailing the procedure for calculating the reorganization energy and the free energy change of the reaction.

A. Key concepts in electron transfer theory

We consider the typical ET in a weakly coupled donor-acceptor complex (the solute) in a polar solvent. The solute has charge distribution $\hat{\rho}_c^{(R)}(\mathbf{r})$ in the reactant state and $\hat{\rho}_c^{(P)}(\mathbf{r})$ in the product state. The macrostate of the solvent can be described by its electronic polarization $\mathbf{P}_{\rm el}$ and orientational polarization $\mathbf{P}_{\rm or}$. Due to the separation of time scale between the fast-responding electronic polarization and the slow-responding orientational polarization, the ET kinetics is controlled by the thermally induced nonequilibrium reorganization in the solvent orientational polarization. Based on the linear dielectric description for the solvent, the free energies in the reactant and the product charge states relate to the nonequilibrium orientational polarization through two parabolas of equal curvature, as sketched in Fig. 1.

The key insight into the Marcus theory[7,8] is that a thermally activated ET process must satisfy both the Franck-Condon principle and energy conservation. As such, prior to the electron transfer, the solvent orientational polarization must reorganize to a transition state ($\mathcal{T}$) such that the free energy in the reactant state equals the free energy in the product state. The difference in the free energy between the transition state and the reactant equilibrium state ($\mathcal{R}$) defines the activation energy $\Delta G^{\ddagger}$ of the ET process. However, it is generally difficult to directly obtain a simple expression for the orientational polarization at the transition state. Instead, the activation energy is calculated by its relation to the free energy change of the reaction ΔG^0 and the reorganization energy λ through the following expression, based on the double-parabola picture of the free energy surface:

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2, \tag{1}$$

where the free energy change and the reorganization energy are given by

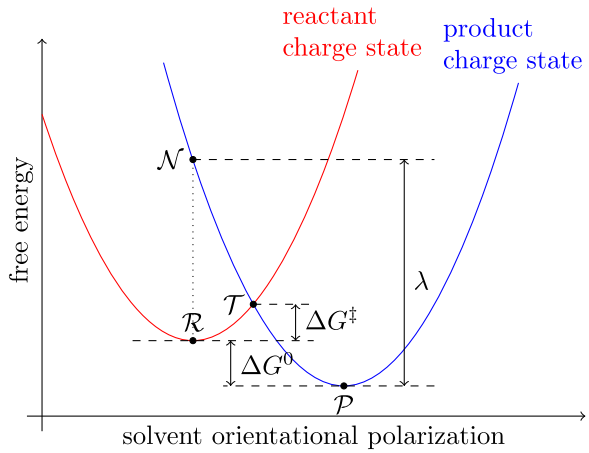

FIG. 1. Free energy vs. solvent orientational polarization for electron transfer reactions. The linear dielectric theory predicts that the two free energy curves are parabolic and have equal curvature. $\mathcal{R}$ and $\mathcal{P}$ are the equilibrium states when the solute is at the reactant charge state and the product charge state, respectively. $\mathcal{N}$ is the nonequilibrium state in which the solute is in the product charge state while the solvent orientational polarization is in equilibrium with the reactant charge state. $\mathcal{T}$ labels the transition state. The activation energy, the free energy change of the reaction, and the reorganization energy are $\Delta G^{\ddagger}$, ΔG^{0}, and λ, respectively.

$$\Delta G^{0} = G_{\mathcal{P}} - G_{\mathcal{R}}, \tag{2}$$

$$\lambda = G_{\mathcal{N}} - G_{\mathcal{P}}. \tag{3}$$

In the above expressions, $G_{\mathcal{S}}$ denotes the free energy of the state $\mathcal{S}$. States $\mathcal{R}$ and $\mathcal{P}$ are the equilibrium states corresponding to the reactant and the product charges, where both the solvent orientational and the electronic polarizations are in full equilibrium with the solute charge. State $\mathcal{N}$ is a nonequilibrium state in which the solute is in the product charge state but the solvent orientational polarization is kept at its previous equilibrium value in state $\mathcal{R}$. In state $\mathcal{N}$, the solvent electronic polarization equilibrates with both the solute charge and the nonequilibrium orientational polarization. These states as well as the relevant energies are indicated in the sketch in Fig. 1.

The usual treatment of reorganization energy in the linear dielectric theory involves the separation of the inner-sphere (solute) and the outer-sphere (solvent) contributions. For an ET process between two simple ions, the coordinated metal complexes, instead of the bare ions, are usually treated as the solute in the inner sphere. For example, for the Fe^{2+}/Fe^{3+} exchange reaction in aqueous medium, the hexaaquocomplexes $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ are considered as the solutes. The inner-sphere reorganization energy considers the nonequilibrium coordinate bond lengths between the ion and the solvent ligands, while the outer-sphere reorganization energy considers nonequilibrium solvent orientational polarization *outside* the hexaaquocomplexes. Using classical linear dielectric theory, Marcus derived the following expression relating the outer-sphere reorganization energy λ_o and the geometry of the solute:[7]

$$\lambda_o = \frac{(\Delta q)^2}{4\pi\epsilon_0}\left(\frac{1}{2a_D} + \frac{1}{2a_A} - \frac{1}{d}\right)\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right), \tag{4}$$

where a_D and a_A are, respectively, the radii of the donor and the acceptor, d is the distance between them, and Δq is the amount of charge transferred. ϵ_∞ and ϵ_s are, respectively, the bulk optical and the static dielectric constants of the solvent. In this work, we refer to the reorganization energy calculated by Eq. (4) as the bulk linear dielectric constant (BLDC) approximation.

The Marcus theory thus establishes that the key to the study of an ET process is to find the free energies of charge solvation under the equilibrium condition, where both the orientational and the electronic polarizations of the solvent are in equilibrium with the solute charge, as well as the nonequilibrium condition, where the solvent orientational polarization is kept at an out-of-equilibrium value. In Subsection II B, we formulate a molecularly based self-consistent-field theory for calculating these free energies.

B. DSCFT for equilibrium and nonequilibrium solvation

In this section, we formulate the DSCFT for charge solvation under both the equilibrium and the nonequilibrium situations. We consider a set of solutes immersed in a polar solvent, as schematically illustrated in Fig. 2. The set of solutes is modeled as a charge distribution $\hat{\rho}_c(\mathbf{r})$ inside some solute cavity C representing the space inaccessible to solvent molecules. The solvent consists of N dipolar molecules, each characterized by its molecular volume v, permanent dipole $\bar{\mu}$, and polarizability α. The state of the ith solvent molecule is described by $\{\mathbf{r}_i, \boldsymbol{\mu}_i, \mathbf{p}_i\}$, which, respectively, denotes its position, permanent dipole (with magnitude $|\boldsymbol{\mu}_i| = \bar{\mu}$), and induced dipole.

We write the total charge density of the solute-solvent system as

$$\hat{\rho}(\mathbf{r}) = \hat{\rho}_c(\mathbf{r}) + \hat{\rho}_{\text{or}}(\mathbf{r}) + \hat{\rho}_{\text{el}}(\mathbf{r}), \tag{5}$$

where $\hat{\rho}_{\text{or}}$ and $\hat{\rho}_{\text{el}}$ are, respectively, the charge densities due to the orientational and the electronic polarizations. As the solvent orientational polarization is due to the permanent dipole moments that are related to the nuclear degrees of freedom, and the electronic polarization is due to the induced dipole moments that are related to the electronic degrees of

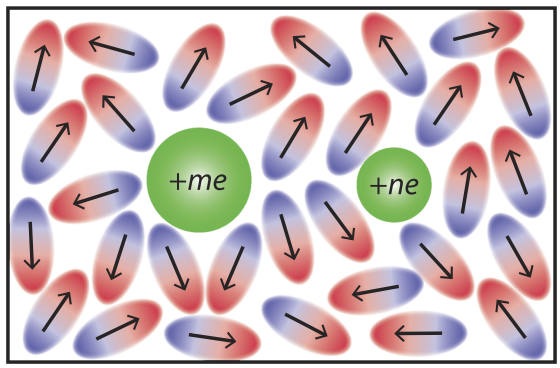

FIG. 2. A schematic representation of the system of solutes in a dipolar solvent. The solute cavity C is represented in green and the solvent is represented by the red and blue dipoles.

freedom, we express $\hat{\rho}_{\rm or}$ and $\hat{\rho}_{\rm el}$ in terms of their corresponding dipole moments as[58]

$$\hat{\rho}_{\rm or}(\mathbf{r}) = -\sum_{i=1}^{N} \boldsymbol{\mu}_i \cdot \nabla\delta(\mathbf{r}-\mathbf{r}_i), \tag{6}$$

$$\hat{\rho}_{\rm el}(\mathbf{r}) = -\sum_{i=1}^{N} \mathbf{p}_i \cdot \nabla\delta(\mathbf{r}-\mathbf{r}_i). \tag{7}$$

The energy of the system consists of the Coulomb interaction and the deformation energy of the induced dipoles, and it can be expressed as

$$U = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{\hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} + \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2\alpha}, \tag{8}$$

where the second term is the deformation energy of the induced dipoles in the harmonic approximation.[58,59] For convenience, we work in a semi-grand canonical ensemble of open-solvent and incompressible system with volume V, temperature T, and solvent chemical potential μ, for which the partition function is

$$\Xi = \sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{N!}\left(\prod_{i=1}^{N}\frac{1}{\eta}\int d\mathbf{r}_i\int d\boldsymbol{\mu}_i\int d\mathbf{p}_i\right) \times \delta[v\hat{n}(\mathbf{r})-1]e^{-\beta U}, \tag{9}$$

where $\beta = 1/k_BT$ and η is the analog of thermal de Broglie wavelength that makes the configurational integral dimensionless. The actual value of η is inconsequential as it only contributes to a reference energy. $\delta[f(\mathbf{r})]$ is the δ-functional, which is the generalization of the Dirac delta function to the function space, such that $\delta[f(\mathbf{r})] = 0$ unless $f = 0$ for all $\mathbf{r}$, and the integral of the functional over the function space satisfies $\int \mathcal{D}f\delta[f(\mathbf{r})] = 1$. $\hat{n}(\mathbf{r}) = \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)$ is the number density operator for the solvent molecules. Rather than accounting for the non-electrostatic interactions between the solvent molecules explicitly, in our coarse-grained approach, we treat the liquid as incompressible and use the δ-functional constraint to enforce a constant density everywhere in the system. The integral runs over the configurational space of solvent molecules, and the integral over $\boldsymbol{\mu}_i$ runs over the 4π solid angle as the magnitude of the permanent dipole is fixed.

Next, we transform the particle-based partition function in Eq. (9) into a field representation by performing a series of identity transformations.[60] This process introduces coarse-grained particle densities and coarse-grained potentials that decouple the particle-particle interactions. These coarse-grained variables are introduced as integration variables using the property of the δ-functional,

$$F[f(\mathbf{r})] = \int \mathcal{D}g\,\delta[f(\mathbf{r})-g(\mathbf{r})]F[g(\mathbf{r})], \tag{10}$$

where f represents a general function and F is a general functional. The δ-functionals can be further rewritten using its Fourier representation,

$$\delta[f] = \int \mathcal{D}h\,\exp\left[i\int d\mathbf{r}\,h(\mathbf{r})f(\mathbf{r})\right]. \tag{11}$$

The resulting partition function after the transformations is

$$\Xi = \int\mathcal{D}w\int\mathcal{D}\rho_{\rm or}\int\mathcal{D}\rho_{\rm el}\int\mathcal{D}w_{\rm or}\int\mathcal{D}w_{\rm el}\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{N!}\left(\prod_{i=1}^{N}\frac{1}{\eta}\int d\mathbf{r}_i\int d\boldsymbol{\mu}_i\int d\mathbf{p}_i\right) \times \exp\left[i\int d\mathbf{r}w(\mathbf{r})[vn(\mathbf{r})-1] - \frac{\beta}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} - \sum_{j=1}^{N}\frac{\beta\mathbf{p}_j^2}{2\alpha} + i\int d\mathbf{r}\,w_{\rm or}(\mathbf{r})\rho_{\rm or}(\mathbf{r}) + i\int d\mathbf{r}\,w_{\rm el}(\mathbf{r})\rho_{\rm el}(\mathbf{r}) - i\int d\mathbf{r}\,w_{\rm or}(\mathbf{r})\hat{\rho}_{\rm or}(\mathbf{r}) - i\int d\mathbf{r}\,w_{\rm el}(\mathbf{r})\hat{\rho}_{\rm el}(\mathbf{r})\right], \tag{12}$$

where $\rho(\mathbf{r}) = \hat{\rho}_c(\mathbf{r}) + \rho_{\rm or}(\mathbf{r}) + \rho_{\rm el}(\mathbf{r})$. The procedure introduces the coarse-grained orientational and electronic charge densities $\rho_{\rm or}$ and $\rho_{\rm el}$ (represented without a hat) that do not depend explicitly on the solvent microscopic configuration. The identity transformation decouples the interaction terms and makes the partition function into one of the single-particles in effective fluctuating fields. Integration over the microscopic configurational space $\{\mathbf{r}_i, \boldsymbol{\mu}_i, \mathbf{p}_i\}$ leads to the field-theoretic grand partition function, given by

$$\Xi = \int\mathcal{D}w\int\mathcal{D}\rho_{\rm or}\int\mathcal{D}\rho_{\rm el}\int\mathcal{D}w_{\rm or}\int\mathcal{D}w_{\rm el}\,e^{-\beta H} \tag{13}$$

with the field Hamiltonian

$$\beta H[w,\rho_{\rm or},\rho_{\rm el},w_{\rm or},w_{\rm el}] = i\int d\mathbf{r}\,w(\mathbf{r}) - i\int d\mathbf{r}\,w_{\rm or}(\mathbf{r})\rho_{\rm or}(\mathbf{r}) - i\int d\mathbf{r}\,w_{\rm el}(\mathbf{r})\rho_{\rm el}(\mathbf{r}) + \int d\mathbf{r}\int d\mathbf{r}'\frac{\beta\rho(\mathbf{r})\rho(\mathbf{r}')}{8\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} - e^{\beta\mu}Q[w,w_{\rm or},w_{\rm el}], \tag{14}$$

where $Q[w,w_{\rm or},w_{\rm el}]$ is the single-particle partition function under the fluctuating fields given by

$$Q[w,w_{\rm or},w_{\rm el}] = \frac{4\pi\bar{\mu}^2}{\eta}\left(\frac{2\pi\alpha}{\beta}\right)^{\frac{3}{2}}\int d\mathbf{r}\left\{\Gamma(\mathbf{r})\frac{\sin(\bar{\mu}|\nabla w_{\rm or}(\mathbf{r})|)}{\bar{\mu}|\nabla w_{\rm or}(\mathbf{r})|} \times \exp\left[iv w(\mathbf{r}) - \frac{\alpha}{2\beta}(\nabla w_{\rm el}(\mathbf{r}))^2\right]\right\}. \tag{15}$$

Here, $\Gamma(\mathbf{r})$ serves to limit the integration to space outside of the cavity, with $\Gamma(\mathbf{r}) = 0$ if $\mathbf{r} \in C$ and $\Gamma(\mathbf{r}) = 1$ otherwise.

The functional integration in the field-theoretic partition function in Eq. (13) cannot be evaluated in closed form. To proceed, we make the saddle-point approximation by taking the maximum of the integrand corresponding to the set of functions $\{w^*, \rho^*_{\mathrm{or}}, \rho^*_{\mathrm{el}}, w^*_{\mathrm{or}}, w^*_{\mathrm{el}}\}$ that extremizes the Boltzmann factor $\exp(-\beta H)$, i.e., $\Xi \approx \exp\{-H[w^*, \rho^*_{\mathrm{or}}, \rho^*_{\mathrm{el}}, w^*_{\mathrm{or}}, w^*_{\mathrm{el}}]\}$. At equilibrium, the saddle-point values of the functional arguments are determined by extremizing H with respect to all of its functional variables. Under the nonequilibrium condition where electronic polarization can respond but the orientational polarization is kept at its previous equilibrium value, we extremize H with respect to all functional variables except ρ_{or} and its conjugate field w_{or}. We delegate the details of the extremization procedure to Appendix A. Here, we simply write down the two sets of resulting constitutive relations, one set applicable under equilibrium conditions, and the other set applicable under nonequilibrium conditions. Since the saddle-point values of the functional variables lie on the imaginary axis, in order to work with real quantities and for the convenience of relating our theory to the classical electrostatics theory, we make a change of variables $w_{\mathrm{or}} = -i\beta\phi_{\mathrm{or}}$, $w_{\mathrm{el}} = -i\beta\phi_{\mathrm{el}}$, and $w = i\beta u$.[61] Upon simplification and rearrangement of the resulting equations, the set of constitutive relations for equilibrium is

$$\nabla \cdot \mathbf{D} = \hat{\rho}_c(\mathbf{r}), \tag{16a}$$

$$\chi_{\mathrm{or}}(\mathbf{r}) = \Gamma(\mathbf{r})\frac{\beta\bar{\mu}^2}{\epsilon_0 v} e^{-\beta v u(\mathbf{r}) + \frac{\beta\alpha}{2}|\nabla\phi(\mathbf{r})|^2} G(\beta\bar{\mu}|\nabla\phi(\mathbf{r})|), \tag{16b}$$

$$\chi_{\mathrm{el}}(\mathbf{r}) = \Gamma(\mathbf{r})\frac{\alpha}{\epsilon_0 v}, \tag{16c}$$

$$1 = e^{-\beta v u(\mathbf{r}) + \frac{\beta\alpha}{2}|\nabla\phi(\mathbf{r})|^2}\frac{\sinh(\beta\bar{\mu}|\nabla\phi(\mathbf{r})|)}{\beta\bar{\mu}|\nabla\phi(\mathbf{r})|}, \tag{16d}$$

where $G(x) = [1/\tanh(x) - 1/x]\sinh(x)/x^2$. $\mathbf{D}$ is the electric displacement given by $\mathbf{D} = -\epsilon_0[1 + \chi_{\mathrm{el}} + \chi_{\mathrm{or}}(\mathbf{r})]\nabla\phi(\mathbf{r})$, and χ_{or} and χ_{el} are, respectively, the orientational and electronic electric susceptibilities. χ_{or} and χ_{el} are zero inside the solute cavity, which is a vacuum with no solvent. The electric susceptibilities relate to the local static dielectric function $\varepsilon_s(\mathbf{r})$ and the local optical dielectric function $\varepsilon_\infty(\mathbf{r})$ through $\varepsilon_s(\mathbf{r}) = 1 + \chi_{\mathrm{or}}(\mathbf{r}) + \chi_{\mathrm{el}}(\mathbf{r})$ and $\varepsilon_\infty(\mathbf{r}) = 1 + \chi_{\mathrm{el}}(\mathbf{r})$. At the saddle-point level, the bulk dielectric constant is only accounted for in the limit of dilute gases, but the effect of this approximation is inconsequential as the solvation energy is determined by the local dielectric response and not directly related to the bulk dielectric constant.[57] We have dropped the superscripts * in these equations for notational simplicity, but it should be understood that the effective charge densities and potentials are at their saddle-point values. The subscripts on the electric potentials are dropped because $\phi(\mathbf{r}) = \phi_{\mathrm{el}}(\mathbf{r}) = \phi_{\mathrm{or}}(\mathbf{r})$ from the minimization of H, as evident from Eqs. (A2) and (A3).

For nonequilibrium situations, the constitutive relations become

$$\nabla \cdot \mathbf{D} = \hat{\rho}_c(\mathbf{r}), \tag{17a}$$

$$\chi_{\mathrm{el}}(\mathbf{r}) = \Gamma(\mathbf{r})\frac{\alpha}{\epsilon_0 v}, \tag{17b}$$

$$1 = e^{-\beta v u(\mathbf{r}) + \frac{\beta\alpha}{2}|\nabla\phi_{\mathrm{el}}(\mathbf{r})|^2}\frac{\sinh(\beta\bar{\mu}|\nabla\phi_{\mathrm{or}}(\mathbf{r})|)}{\beta\bar{\mu}|\nabla\phi_{\mathrm{or}}(\mathbf{r})|}, \tag{17c}$$

where the values of ϕ_{or} and χ_{or} for the nonequilibrium state $\mathcal{N}$ are from their values at the reactant equilibrium state $\mathcal{R}$. The electric displacement is given by $\mathbf{D} = -\epsilon_0(1 + \chi_{\mathrm{el}})\nabla\phi_{\mathrm{el}}(\mathbf{r}) - \epsilon_0\chi_{\mathrm{or}}(\mathbf{r})\nabla\phi_{\mathrm{or}}(\mathbf{r})$, since ϕ_{or} and ϕ_{el} must now be distinguished because the relation $\phi_{\mathrm{or}} = \phi_{\mathrm{el}}$ no longer holds under the nonequilibrium condition.

The free energy of solvation can be obtained by substituting the saddle-point values of the functional arguments into the Hamiltonian in Eq. (14). Upon simplification, for which the details are given in Appendix A, the free energy of solvation is written as

$$G[\mathbb{C}, \hat{\rho}_c(\mathbf{r})] = \int d\mathbf{r}\left\{\frac{1}{2}\epsilon_0(1 + \chi_{\mathrm{el}}(\mathbf{r}))|\nabla\phi_{\mathrm{el}}(\mathbf{r})|^2 + \epsilon_0\chi_{\mathrm{or}}(\mathbf{r})|\nabla\phi_{\mathrm{or}}(\mathbf{r})|^2 - \frac{1}{\beta v}\Gamma(\mathbf{r})\log\left[\frac{\sinh\beta\bar{\mu}|\nabla\phi_{\mathrm{or}}(\mathbf{r})|}{\beta\bar{\mu}|\nabla\phi_{\mathrm{or}}(\mathbf{r})|}\right] - \frac{1}{\beta v}\Gamma(\mathbf{r})\right\}, \tag{18}$$

where $\mathbb{C} = \{\chi_{\mathrm{or}}, \phi_{\mathrm{or}}, \Gamma\}$ is the nuclear configuration set that contain all necessary information describing the nuclear configuration, and χ_{el} and ϕ_{el} are calculated using the constitutive relations. The saddle-point free energy as an integral over the whole space is infinite, but the divergent parts cancel in the evaluation of reorganization energy as presented in Appendix B.

It is known that field-theoretic treatment of electrostatically interacting systems at the saddle-point level leads to the Poisson equation, as in Eqs. (16a) and (17a).[57,62,63] The spatially varying orientational and electronic electric susceptibilities $\chi_{\mathrm{or}}(\mathbf{r})$ and $\chi_{\mathrm{el}}(\mathbf{r})$ describe the collective response of the permanent dipoles and the induced dipoles, respectively, given by Eqs. (16b), (16c), and (17b). The equations for electric susceptibilities are equivalent to the nonlinear Langevin-Debye model when the field $-\nabla\phi$ is taken as the local field.[64–67] The incompressibility condition is accounted for at the mean-field level by Eqs. (16d) and (17c). Eqs. (16)–(18) are the key equations in the DSCFT. In Sec. II C, we apply the DSCFT to a simple ET process between two ions and present results of our numerical calculations.

C. Application of DSCFT to simple electron transfer between two ions

In this section, we apply the DSCFT framework to a simple ET reaction $D^m + A^n \rightarrow D^{m+1} + A^{n-1}$ between two ions. Following Marcus's two-sphere model, the donor (D)

and the acceptor (A) are modeled as two spherical cavities, each with a point charge at the center. The reactant state has charge distribution $\hat{\rho}_c^{(R)}(\mathbf{r}) = me\delta(\mathbf{r}-\mathbf{R}_D) + ne\delta(\mathbf{r}-\mathbf{R}_A)$, and the product state has charge distribution $\hat{\rho}_c^{(P)}(\mathbf{r}) = (m+1)e\delta(\mathbf{r}-\mathbf{R}_D) + (n-1)e\delta(\mathbf{r}-\mathbf{R}_A)$, where $\mathbf{R}_D$ and $\mathbf{R}_A$ are, respectively, the positions of the donor and the acceptor, and e is the elementary charge. The distance between the donor and the acceptor is $d = |\mathbf{R}_D - \mathbf{R}_A|$. The solute cavity $C_{\mathcal{S}}(\mathcal{S} = \mathcal{P}, \mathcal{R}, \mathcal{N})$ is represented by the set $\{\mathbf{r} : |\mathbf{r}-\mathbf{R}_D| < a_D^{\mathcal{S}}$ or $|\mathbf{r}-\mathbf{R}_A| < a_A^{\mathcal{S}}\}$, where $a_D^{\mathcal{S}}$ and $a_A^{\mathcal{S}}$ are, respectively, the radii of the species D and A in state $\mathcal{S}$.[68] For the equilibrium state $\mathcal{R}/\mathcal{P}$, $a_D^{\mathcal{R}/\mathcal{P}}$ and $a_A^{\mathcal{R}/\mathcal{P}}$ are taken to be the ionic radii of D^m/D^{m+1} and A^n/A^{n-1}, respectively. For the nonequilibrium state $\mathcal{N}$, the solute cavity takes the ionic radii of the species in state $\mathcal{R}$, such that $a_{D/A}^{\mathcal{N}} = a_{D/A}^{\mathcal{R}}$, because states $\mathcal{N}$ and $\mathcal{R}$, having the same solvent nuclear configuration, have the same region inaccessible to the solvent. $\Gamma^{\mathcal{S}}(\mathbf{r})$, the indicator function of the solute cavity $C_{\mathcal{S}}$, equals 0 when $\mathbf{r} \in C_{\mathcal{S}}$ and 1 otherwise.

Under a particular distribution of the solute charge, the nonequilibrium free energy can be evaluated with respect to the free energy at the equilibrium state for the same solute charge distribution. In doing so, the free energy surface $G^{(R)}$ in the reactant charge state and the free energy surface $G^{(P)}$ in the product charge state are expressed as

$$G^{(R)} = G[\mathbb{C}, \hat{\rho}_c^{(R)}] - G_{\text{eq}}^{(R)}, \tag{19}$$

$$G^{(P)} = G[\mathbb{C}, \hat{\rho}_c^{(P)}] - G_{\text{eq}}^{(P)} + \Delta G^0, \tag{20}$$

where ΔG^0 is the free energy change of the reaction. $G_{\text{eq}}^{(R)}$ and $G_{\text{eq}}^{(P)}$ are the free energies at the equilibrium states $\mathcal{R}$ and $\mathcal{P}$, respectively, given by $G_{\text{eq}}^{(R)} = G[\mathbb{C}^{\mathcal{R}}, \hat{\rho}_c^{(R)}]$ and $G_{\text{eq}}^{(P)} = G[\mathbb{C}^{\mathcal{P}}, \hat{\rho}_c^{(P)}]$, where $\mathbb{C}^{\mathcal{S}} = \{\chi_{\text{or}}^{\mathcal{S}}, \phi_{\text{or}}^{\mathcal{S}}, \Gamma^{\mathcal{S}}\}$ $(\mathcal{S} = \mathcal{R}, \mathcal{P})$ is the nuclear configuration set of state $\mathcal{S}$. $\chi_{\text{or}}^{\mathcal{R}}$, $\phi_{\text{or}}^{\mathcal{R}}$, and $\Gamma^{\mathcal{R}}$ are the values of χ_{or}, ϕ_{or}, and Γ in the reactant equilibrium state $\mathcal{R}$; $\chi_{\text{or}}^{\mathcal{P}}$, $\phi_{\text{or}}^{\mathcal{P}}$, and $\Gamma^{\mathcal{P}}$ are defined similarly. The reorganization energy λ is then

$$\lambda = G[\mathbb{C}^{\mathcal{R}}, \hat{\rho}_c^{(P)}] - G[\mathbb{C}^{\mathcal{P}}, \hat{\rho}_c^{(P)}]. \tag{21}$$

A strategy for evaluating λ is presented in Appendix B, where allowance is made for the solute cavities in the reactant and the product states to be different (i.e., $\Gamma^{\mathcal{R}} = \Gamma^{\mathcal{P}}$ is not required).

To simplify the calculation further, we approximate the solution to Eqs. (16a) and (17a) by assuming that the electric displacement $\mathbf{D}$ can be written as the superposition of the displacement due to each individual point charge as [69]

$$\mathbf{D}(\mathbf{r}) = \frac{q_D}{4\pi r_D^2}\hat{\mathbf{r}}_D + \frac{q_A}{4\pi r_A^2}\hat{\mathbf{r}}_A, \tag{22}$$

where q_D and q_A are the charges on the donor and the acceptor, respectively, $\mathbf{r}_{D/A} = \mathbf{r} - \mathbf{R}_{D/A}$ and $\hat{\mathbf{r}}_{D/A}$ indicates the unit vector in the direction of $\mathbf{r}_{D/A}$. We expect that the error due to this approximation is small, as the jump in dielectric constant at the boundary of the solute cavity is not significant because of dielectric saturation.

For each state, we perform numerical calculations on a bispherical coordinate (σ, τ, φ), which is related to the cylindrical coordinate (r, z, φ) by $z = a_0 \sinh\sigma/(\cosh\sigma - \cos\tau)$ and $r = a_0 \sin\tau/(\cosh\sigma - \cos\tau)$.[70] Each constant-$\sigma$ surface in the bispherical coordinate is circle of radius $a_0/|\sinh\sigma|$ with its center located at $z = a_0 \coth\sigma$. The value of a_0 is determined by the ionic radii of the donor and the acceptor and their distance, and by requiring that the cavity boundaries of the donor and the acceptor are each a surface of constant σ, and that the region accessible by the solvent is simply described by $\sigma_A < \sigma < \sigma_D$. This is achieved by simultaneously solving

$$\frac{a_0}{|\sinh\sigma_D|} = a_D, \tag{23a}$$

$$\frac{a_0}{|\sinh\sigma_A|} = a_A, \tag{23b}$$

$$a_0 \coth\sigma_D - a_0 \coth\sigma_A = d. \tag{23c}$$

That is, the donor cavity surface is $\sigma = \sigma_D = \cosh^{-1}\left(\frac{a_D^2 - a_A^2 + d^2}{2a_D d}\right)$, and the acceptor cavity surface is $\sigma = \sigma_A = -\cosh^{-1}\left(\frac{a_A^2 - a_D^2 + d^2}{2a_A d}\right)$, and $a_0 = a_D \sinh\sigma_D$. Due to the cylindrical symmetry in the problem, we only have to perform calculations on the two-dimensional $\sigma\tau$-plane. The integration for the free energy is carried out on a 240×680 $\sigma\tau$-grid between $\sigma \in (\sigma_A, \sigma_D)$ and $\tau \in (0, \pi)$. The potential ϕ in the equilibrium state is found by iteration until the next iteration produces a reduced electric field $\nabla\phi/[\frac{e}{4\pi\epsilon_0(2a_D a_A/(a_D+a_A))}]$ within 10^{-6} from its current value at all grid points.

III. RESULTS AND DISCUSSIONS

In this section, we consider ET reactions in water, for which the molecules have a vacuum permanent dipole moment $\bar{\mu} = 1.85$ D, polarizability $\alpha = 1.45$ Å^3, and molecular volume $v = 30.0$ Å^3. The temperature is $T = 298.15$ K. Here, we consider self-exchange reactions, which involves only two species before and after the reaction, and thus, we simplify the notation for the solute radii as $a_D = a_D^{\mathcal{R}} = a_A^{\mathcal{P}}$ and $a_A = a_A^{\mathcal{R}} = a_D^{\mathcal{P}}$.

A. A unified description of solvent molecules

As a first step, we evaluate the outer-sphere solvent reorganization energy using the DSCFT for the Fe^{2+}/Fe^{3+} exchange reaction. We set the radii of the solute cavities to be $a_D = 3.31$ Å and $a_A = 3.18$ Å, which are the radii of $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$, respectively.[71] We note that in the product equilibrium state $\mathcal{P}$, the radii of the ET species are switched. For self-exchange reactions, the reorganization energy can be calculated as the free energy difference between the nonequilibrium state $\mathcal{N}$ and reactant equilibrium state $\mathcal{R}$, both involving the same nuclear configuration, and thus the same solvent accessible space. At the contact distance of $d = 6.5$ Å between the two spherical ions, the DSCFT predicts the outer-sphere solvent reorganization to be 26.2 kcal/mol, in good agreement with the earlier value of 27.6 kcal/mol given in the literature.[3]

Even though the separation of the inner- and the outer-sphere contributions is a widely used strategy for evaluating reorganization energies, the discrimination between

the inner- and the outer-sphere molecules introduces additional parameters to the theory. Furthermore, the treatment ignores dipolar interactions between the inner- and the outer-sphere solvent molecules. In contrast, MD simulations do not distinguish between the inner- and the outer-sphere molecules — the same forcefield is used on all solvent molecules, regardless of their distances from the ions. A theory based on molecular-level interactions around the ions should be able to treat all solvent molecules on equal footing. Since the DSCFT is able to account for the spatial variation in the solvent response at the molecular length scale, we expect that distinction of the inner- and the outer-sphere solvent molecules may not be necessary, and the reorganization energy due to *all* solvent molecules can be directly evaluated.

To test how well the DSCFT can predict the reorganization energy by treating all solvent molecules in a unified manner, we calculate the *total* reorganization energy for a variety of ET reactions between simple ions. We set the cavity radii a_D and a_A to be the crystal ionic radii of the donor and the acceptor and use earlier literature values of the donor-acceptor distance for the value of d. Table I tabulates the reorganization energy and the activation energy for selected ET reactions calculated by the DSCFT, together with values from earlier calculations in the literature that treat the inner- and outer-sphere reorganization energies separately, as well as values obtained from experiments.[72] In reality, the electron transfer occurs at a range of donor-acceptor separation d (e.g., around 4.5 Å to 5.5 Å for Fe^{2+}/Fe^{3+} exchange),[73] and thus, the comparison between the calculated value based on a typical value of d within this range and the experimentally measured values serves only to provide qualitative validation of our approach. We observe that the activation energies calculated using the DSCFT are generally within a few kilocalorie per mole from literature values. This suggests that the DSCFT, with readily available parameters describing the solvent and the solutes, can make reliable predictions for the direct evaluation of the *total* reorganization energy by a unified treatment of the inner-sphere and the outer-sphere solvent molecules. We note in addition that, even though explicit solvent structure and molecular specific interactions have not been taken into account in the DSCFT, the DSCFT predicts the value of 20.3 kcal/mol for ET activation energy for Fe^{2+}/Fe^{3+} exchange in water, in excellent agreement with the value of 20 kcal/mol from atomistic simulations by Kuharski *et al.*[26]

Some ionic solutes have a high-spin state and a low-spin state. It has been proposed that spin-exchange may couple to ET reactions, such that the less prevalent spin state serves as the reaction intermediate.[77] Therefore, for ionic species that have a high-spin state and a low-spin state, we calculate the activation energy of electron transfer for both the high-spin and the low-spin species. For the Fe^{2+}/Fe^{3+} exchange, the Co^{2+}/Co^{3+} exchange, and the Mn^{2+}/Mn^{3+} exchange considered in this work, we found that the ET processes between ions of low-spin states have lower activation energies than those between ions in the high-spin state. By comparing the calculated ET activation energies and the experimentally obtained value, our result suggests that the Mn^{2+}/Mn^{3+} exchange may primarily occur between the low-spin Mn^{2+} and Mn^{3+}, as the experimentally obtained activation energy is comparable to the DSCFT-calculated activation energy between the low-spin Mn^{2+} and Mn^{3+}. For the Fe^{2+}/Fe^{3+}

TABLE I. The DSCFT-calculated reorganization energy λ_{DSCFT} and activation energy $\Delta G^{\ddagger}_{\mathrm{DSCFT}}$, as well as the total activation energy $\Delta G^{\ddagger}_{\mathrm{cal}}$ from earlier calculations in the literature that treat the inner- and outer-sphere reorganization energies separately, and the experimentally obtained activation energy $\Delta G^{\ddagger}_{\mathrm{exp}}$ for a range of ET reactions. The crystal ionic radii in Ref. 74 are used for the cavity radii of the solutes. High-spin and low-spin species are denoted by hs and ls, respectively.

Donor/acceptor	a_D (Å)	a_A (Å)	d (Å)	λ_{DSCFT} (kcal/mol)	$\Delta G^{\ddagger}_{\mathrm{DSCFT}}$ (kcal/mol)	$\Delta G^{\ddagger}_{\mathrm{cal}}$ (kcal/mol)	$\Delta G^{\ddagger}_{\mathrm{exp}}$ (kcal/mol)
Fe^{2+}/Fe^{3+}(hs)	0.92	0.785	5.25[a]	81.4	20.3	19.3[b],14.8[c]	16.6[b],14.9[c]
Fe^{2+}/Fe^{3+}(ls)	0.75	0.69	5.25[a]	57.2	14.3		
Co^{2+}/Co^{3+}(hs)	0.885	0.75	6.6[d]	90.9	22.7	21.7[d]	16.5[b]
Co^{2+}/Co^{3+}(ls)	0.79	0.685	6.6[d]	87.1	21.8		
Mn^{2+}/Mn^{3+}(hs)	0.97	0.785	5.36[e]	101	25.2	20.2[b]	≥16.6[b]
Mn^{2+}/Mn^{3+}(ls)	0.81	0.72	5.36[e]	70.4	17.6		
V^{2+}/V^{3+}	0.93	0.78	5.33[e]	88.3	22.1	16.7[b]	20.2[b]
Cr^{2+}/Cr^{3+}	0.94	0.755	5.32[e]	106	26.5	20.3[b]	≥23.9[b]
Ru^{2+}/Ru^{3+}	0.87	0.82	6.5[d]	46.3	11.6	10.5[d]	...
Ce^{3+}/Ce^{4+}	1.15	1.01	7.36[b]	75.6	18.9	19.3[b]	19.0[b]
Pu^{3+}/Pu^{4+}	1.14	1.00	7.24[b]	76.3	19.1	20.9[b]	16.3[b]
Pa^{3+}/Pa^{4+}	1.16	1.04	7.34[b]	65.7	16.4	20.4[b]	...
U^{3+}/U^{4+}	1.165	1.03	7.3[b]	71.7	17.9	20.5[b]	...
Am^{3+}/Am^{4+}	1.115	0.99	7.22[b]	71.6	17.9	21.0[b]	...

[a]Reference 75.
[b]Reference 1.
[c]Reference 76.
[d]Reference 3.
[e]Reference 29.

exchange, the experimentally obtained activation energy is in between the DSCFT-calculated activation energies for the high-spin and the low-spin Fe ions; thus, our result suggests that both the exchange between the high-spin ions and the exchange between the low-spin ions occur under experimental conditions. For the Co^{2+}/Co^{3+} exchange, the DSCFT-calculated activation energy, as well as the activation energy calculated in earlier literature, is much higher than the experimentally obtained activation energy. The reason for this may be the presence of an alternative pathway for electron transfer, as discussed in several earlier papers[78,79] and reviewed by Sutin in Ref. 3.

Since the DSCFT is able to compute the all-solvent contribution towards the reorganization energy, we further investigate its dependence on the size of the solutes. In the immediate vicinity of an ion, the effect of dielectric saturation causes the static dielectric constant ϵ_s to approach the optical dielectric constant ϵ_∞, and thus, the Pekar factor $(1/\epsilon_\infty - 1/\epsilon_s)$ in this region is small compared to its bulk value. Such effect of dielectric saturation is not accounted for in the linear dielectric theory, which predict the solvent reorganization energy to be proportional to the Pekar factor of the bulk solvent as given by Eq. (4). When the ionic radius of the solute is small or the charge on the solute is large, the effect of dielectric saturation is significant, and we expect that the actual solvent reorganization energy in these situations will be much smaller than that predicted by the linear dielectric theory.

Here, we compare the solvent reorganization energies calculated using the DSCFT and the BLDC approximation for the reaction $M^m + M^{m+1} \rightarrow M^{m+1} + M^m$ at $m = 0, 1$, and 2. We fix the donor-acceptor distance at $d = 10$ Å and ignore the size difference between the donor and the acceptor by assuming $a_D = a_A = a$. In Fig. 3, we plot the reorganization energy as a function of solute radius a. We observe that the linear dielectric theory works well only for solute radius more than approximately 3.5 Å, comparable to the radii of typical coordinated ion complexes. This is probably the reason for separating the inner- and the outer-sphere treatments for the solvent in the linear dielectric theory, since solvent molecules in the outer-sphere are at a sufficient distance away from the ion to be reasonably treated using bulk linear dielectric constants. For smaller solutes with radii less than 3.5 Å, the reorganization energy not only depends on the amount of charge transferred but also on the magnitude of charge on the solutes, contrary to the prediction of the BLDC approximation. Furthermore, it is intriguing that the solvent reorganization energy for self-exchange between charged solutes stays constant for $a \lessapprox 2.5$ Å, but this effect is absent for the 0/1+ exchange reaction. This can be understood as a manifestation of dielectric saturation — as the orientational dipoles are fully saturated within $a \lessapprox 2.5$ Å from an ion, this saturated region is not much affected if the charge on the ion changes by e, and therefore, the polarization in this region does not contribute to the reorganization energy.

The unified treatment of the inner-sphere and the outer-sphere solvent molecules considerably simplifies the calculation of reorganization energies. Although we have ignored the specific interactions between the ions and their coordinated solvent molecules, by treating the spatially dependent electrostatic interaction between the ions and the solvent molecules, we are able to capture the energetics of the coordination bonds. This is most likely because electrostatic interaction is the main factor in determining the energetics of ion-solvent interactions. We also note that the DSCFT accounts for the excluded volume of the solvent molecules by the incompressibility constraint, and it does not account for the liquid-state packing structure of the solvent molecules. Yet, the previous success of the DSCFT in capturing the equilibrium solvation free energy of ions in both single-component liquids and binary mixtures[57] and the current success in describing the reorganization energy for ET reactions seem to suggest that geometric packing of the solvent, at least for simple molecules, may not be important, due to the long-range nature of the electrostatic interactions, which is not much affected by smearing out the local molecular density.

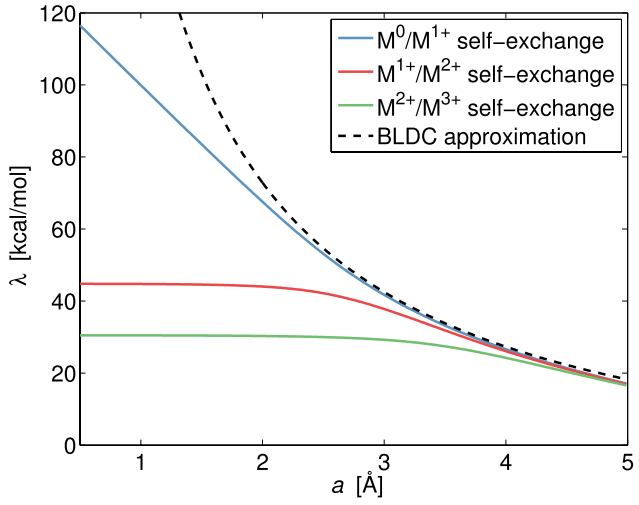

FIG. 3. The reorganization energy λ as a function of the radius of solutes a for fixed interionic separation 10 Å in water. The bulk linear dielectric constant (BLDC) approximation is calculated using Eq. (4), with static dielectric constant $\epsilon_s = 80.1$ and optical dielectric constant $\epsilon_\infty = n^2 = 1.33^2$, where n denotes the refractive index.

B. The nonequilibrium solvation free energy surface

A consequence of the linear dielectric description for the solvent is that the nonequilibrium free energy surfaces in the reactant and the product charge states are two parabolas of equal curvature. This leads to Eq. (1), a simple relationship between the activation energy and the reorganization energy, and Eq. (4), the prediction that the solvent reorganization energy depends on the amount of charge transfer but not on the magnitude of charge on the electron-transferring species. In this section, we apply the DSCFT to calculate the nonequilibrium free energy surface as a function of the reaction coordinate and explore the alterations to predictions of the linear dielectric theory as a result of a more refined description of solvent response.

We calculate the free energy surfaces for two model reactions of the form $M^m + M^n \rightarrow M^{m+1} + M^{n-1}$ with (i) $m = +2$ and $n = +3$ and (ii) $m = 0$ and $n = +1$. For simplicity, we set the radii of all solute species to be $a = 1$ Å, regardless of their charge states, so that $\Gamma(\mathbf{r})$ is independent of the states.

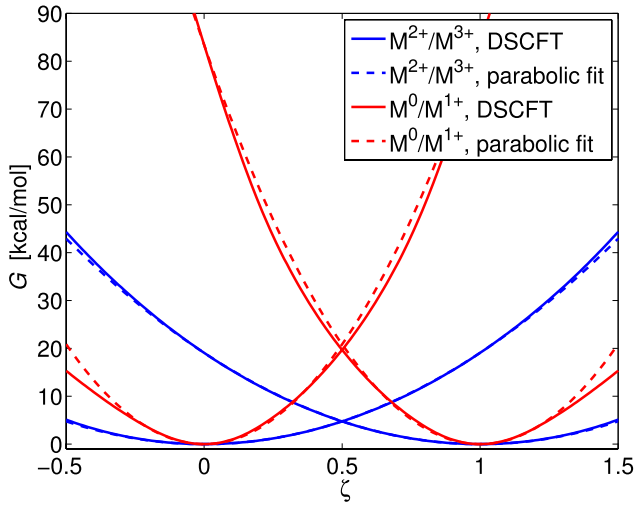

FIG. 4. Free energy curves vs. the charging parameter ζ for self-exchange reactions. Each dashed line is a parabolic fit to the corresponding free energy curve that passes through the values of $G(\zeta = 0)$ and $G(\zeta = 1)$.

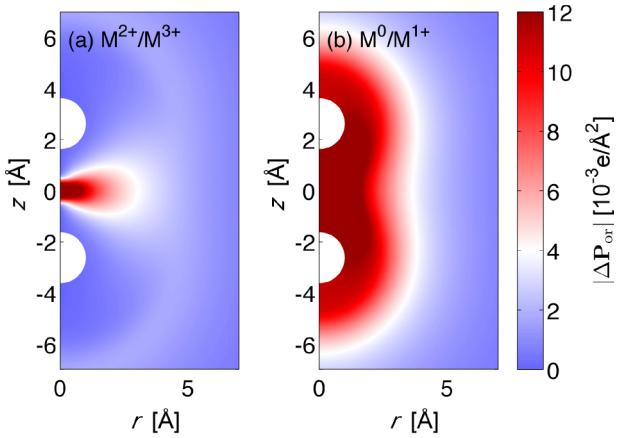

FIG. 5. The magnitude of change in the orientational polarization $|\Delta \mathbf{P}_{or}|$ between the reactant and the product equilibrium states for (a) the M^{2+}/M^{3+} exchange reaction and (b) the M^{0}/M^{1+} exchange reaction. The values of polarization change have unit $10^{-3}\, e/\text{Å}^2$ on a cross section around the donor and the acceptor in the cylindrical coordinate.

The distance between the donor and the acceptor is set to be $d = 5.25$ Å apart. It is common to calculate the free energy as a function of a charging parameter ζ, with $\chi_{or}(\zeta)$ and $\phi_{or}(\zeta)$ representing the equilibrium value of χ_{or} and ϕ_{or} when the solute is $M^{m+\zeta} + A^{n-\zeta}$. We write $G^{(R)}$ and $G^{(P)}$ as a function of ζ as

$$G^{(R)}(\zeta) = G[\mathbb{C}(\zeta), \hat{\rho}_c^{(R)}] - G_{eq}^{(R)}, \tag{24}$$

$$G^{(P)}(\zeta) = G[\mathbb{C}(\zeta), \hat{\rho}_c^{(P)}] - G_{eq}^{(P)} + \Delta G^o, \tag{25}$$

where $\mathbb{C}(\zeta) = \{\chi_{or}(\zeta), \phi_{or}(\zeta), \Gamma\}$.

In Fig. 4, we plot $G^{(R)}(\zeta)$ and $G^{(P)}(\zeta)$ for the exchange reactions between M^{2+} and M^{3+} and between M^0 and M^{1+}. We note that for both reactions, the free energy curves are well represented as parabolas in the relevant part of the reaction coordinate. This is because, for a self-exchange reaction, anharmonicity in solvent response cancels out due to the symmetry of the reaction.[9] Our result is in agreement with earlier MD simulations, which have also found the parabolic free energy surfaces to be a good description for self-exchange reactions.[26,80]

However, the curvature of the free energy parabola depends strongly on the charge on the electron-transferring species, contrary to the prediction of linear dielectric theory. The reorganization energy for the electron exchange between M^0 and M^{1+} is larger than that between M^{2+} and M^{3+} by about a factor of four. Our results are consistent with earlier findings in molecular simulations of ET reaction in nonpolarizable solvents.[17,18]

We expect that the change in the solvent orientational polarization between the reactant and the product states is a key factor determining the magnitude of reorganization energy. To gain insight on how the reorganization energy depends on the charge of the solutes, we examine the change in the solvent orientational polarization $\Delta \mathbf{P}_{or}$ between the reactant and the product equilibrium states given by

$$\begin{aligned}\Delta \mathbf{P}_{or} &= \mathbf{P}_{or,eq}^{(P)} - \mathbf{P}_{or,eq}^{(R)} \\ &= -\epsilon_0 \chi_{or}^{\mathcal{P}} \nabla \phi_{or}^{\mathcal{P}} + \epsilon_0 \chi_{or}^{\mathcal{R}} \nabla \phi_{or}^{\mathcal{R}},\end{aligned} \tag{26}$$

where $\mathbf{P}_{or,eq}^{(R)}$ and $\mathbf{P}_{or,eq}^{(P)}$ denote the equilibrium solvent orientational polarization in the reactant and the product charge states. Fig. 5 plots the spatial variation of $|\Delta \mathbf{P}_{or}|$ around the donor and the acceptor. As suggested by the figure, the change in orientational polarization in the M^0/M^{1+} exchange reaction is more substantial in magnitude and more extensive in space than that in the M^{2+}/M^{3+} reaction, resulting in the larger reorganization energy in the M^0/M^{1+} exchange reaction.

IV. CONCLUSIONS

Using field-theoretic techniques, we have developed a DSCFT for treating charge solvation under both equilibrium and nonequilibrium conditions and applied the theory to study solvent reorganization in ET reactions. The central result of the DSCFT consists of two sets of easily solvable constitutive relations, one applicable under the equilibrium condition and the other under the nonequilibrium condition, as well as an expression for the free energy of the system. With readily available parameters, the DSCFT provides a coarse-grained molecular theory for the reorganization energies and activation energies in self-exchange ET reactions.

Because the DSCFT naturally accounts for the spatial variation in the solvent response, it can be used to directly calculate the total solvent reorganization energy without making a distinction between the inner-sphere and outer-sphere solvent molecules. The activation energies of a range of simple ET reactions calculated with the DSCFT are within a few kilocalories per mole from previous calculated or experimentally obtained values. The dependence of the reorganization energy on the size of the solutes suggests that a saturation zone within approximately 2.5 Å from the center of the charged solutes contributes insignificantly to the reorganization energy. In addition, we find that for solutes with radii larger than approximately 3.5 Å, the solvent can be reasonably described by the bulk optical and static dielectric constants. Furthermore, by calculating the free energy landscape for model charge-exchange reactions, we

find that the free energy surfaces are well described by two equal-curvature parabolas. However, contrary to the prediction of linear dielectric theory, the reorganization energy depends strongly on the magnitude of charge on the solutes. In fact, for the geometry considered in this work, there is a four-fold difference between the solvent reorganization energies of the M^0/M^{1+} exchange and the M^{2+}/M^{3+} exchange. This large difference in reorganization energy would be very significant for the kinetics of ET reactions.

We have focused on applying the DSCFT to ET reactions between two simple ions in this article, but the method can be extended to solutes with more complicated geometries, such as multiatom molecules and proteins, by altering the solute charge distribution $\hat{\rho}_c(\mathbf{r})$ and the solute cavity C.[84] Furthermore, while in this work, we have only applied the DSCFT to self-exchange reactions, and the theory can be applied to asymmetric ET reactions where there is a change in charge and/or solute cavity, provided that the free energy change of the reaction ΔG^0 is given. Since the DSCFT makes no assumptions on the form of the reorganization energy, it is a suitable tool for studying nonlinearity and asymmetry in the solvent response for general ET processes.[39] In addition, the framework of the DSCFT can be easily extended to ET reactions in solvent mixtures, where preferential solvation is expected to have significant effects in the solvent reorganization.[57,81–83] We will examine such effects on ET reactions in solvent mixtures in a forthcoming paper.

Finally, we note that while field-theoretical techniques are widely used in soft-matter and polymeric systems, we are not aware of its application to chemical reactions. We believe that the application of field-theoretical techniques to chemical systems is a fruitful direction, particularly in cases where there are a large number of fluctuating environmental degrees of freedom.

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APPENDIX A: EXTREMIZATION OF THE FIELD HAMILTONIAN

Starting from Eq. (14), extremization of H with respect to w, ρ_{or}, ρ_{el}, w_{or}, and w_{el}, respectively, gives

$$1 = \frac{e^{\beta\mu}}{\eta} 4\pi\bar{\mu}^2 \left(\frac{2\pi\alpha}{\beta}\right)^{\frac{3}{2}} v \times e^{ivw(\mathbf{r})} \frac{\sin(\bar{\mu}|\nabla w_{\mathrm{or}}(\mathbf{r})|)}{\bar{\mu}|\nabla w_{\mathrm{or}}(\mathbf{r})|} e^{-\frac{\alpha}{2\beta}(\nabla w_{\mathrm{el}}(\mathbf{r}))^2}, \tag{A1}$$

$$iw_{\mathrm{or}}(\mathbf{r}) = \beta \int d\mathbf{r}' \frac{\hat{\rho}_c(\mathbf{r}') + \rho_{\mathrm{or}}(\mathbf{r}') + \rho_{\mathrm{el}}(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|}, \tag{A2}$$

$$iw_{\mathrm{el}}(\mathbf{r}) = \beta \int d\mathbf{r}' \frac{\hat{\rho}_c(\mathbf{r}') + \rho_{\mathrm{or}}(\mathbf{r}') + \rho_{\mathrm{el}}(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|}, \tag{A3}$$

$$\rho_{\mathrm{or}}(\mathbf{r}) = -i\frac{e^{\beta\mu}}{\eta} 4\pi\bar{\mu}^2 \left(\frac{2\pi\alpha}{\beta}\right)^{\frac{3}{2}} \times \nabla\cdot\left[\Gamma(\mathbf{r}) e^{ivw(\mathbf{r})} e^{-\frac{\alpha}{2\beta}(\nabla w_{\mathrm{el}})^2} \mathcal{G}(\bar{\mu}|\nabla w_{\mathrm{or}}|)\bar{\mu}^2 \nabla w_{\mathrm{or}}\right], \tag{A4}$$

$$\rho_{\mathrm{el}}(\mathbf{r}) = i\frac{e^{\beta\mu}}{\eta} 4\pi\bar{\mu}^2 \left(\frac{2\pi\alpha}{\beta}\right)^{\frac{3}{2}} \left(\frac{\alpha}{\beta}\right) \times \nabla\cdot\left[\Gamma(\mathbf{r}) e^{ivw(\mathbf{r})} e^{-\frac{\alpha}{2\beta}(\nabla w_{\mathrm{el}})^2} \frac{\sin(\bar{\mu}|\nabla w_{\mathrm{or}}|)}{\bar{\mu}|\nabla w_{\mathrm{or}}|} \nabla w_{\mathrm{el}}\right], \tag{A5}$$

where $\mathcal{G}(x) = (1/\tan x - 1/x)(\sin x)/x^2$.

Equation (A1) is obtained by extremizing w outside the solute cavity. Inside the solute cavity where w is not defined, we set $w = 0$. Furthermore, by letting the fields w, w_{or}, and w_{el} go to zero as $|\mathbf{r}| \to \infty$, Eq. (A1) gives

$$1 = \frac{e^{\beta\mu}}{\eta} 4\pi\bar{\mu}^2 \left(\frac{2\pi\alpha}{\beta}\right)^{\frac{3}{2}} v. \tag{A6}$$

Furthermore, Eqs. (A2) and (A3) can be rewritten by taking the Laplacian on both sides of the equation,

$$-i\frac{\epsilon_0}{\beta}\nabla^2 w_{\mathrm{or}}(\mathbf{r}) = \hat{\rho}_c(\mathbf{r}) + \rho_{\mathrm{or}}(\mathbf{r}) + \rho_{\mathrm{el}}(\mathbf{r}), \tag{A7}$$

$$-i\frac{\epsilon_0}{\beta}\nabla^2 w_{\mathrm{el}}(\mathbf{r}) = \hat{\rho}_c(\mathbf{r}) + \rho_{\mathrm{or}}(\mathbf{r}) + \rho_{\mathrm{el}}(\mathbf{r}). \tag{A8}$$

With these, the constitutive relations in Eq. (16) can be derived by noting that Eqs. (A1)–(A5) all hold under the equilibrium condition. On the other hand, Eq. (17) can be derived by noting that ρ_{or} and w_{or} are out of equilibrium under the nonequilibrium condition, and therefore, only Eqs. (A1), (A3), and (A5) hold.

To derive the saddle-point free energy, we substitute the nonequilibrium set of constitutive relations and the out-of-equilibrium value of ρ_{or} into the field Hamiltonian in Eq. (14). Following integration by parts, we arrive at

$$\begin{aligned} G &= \int d\mathbf{r} \left\{\frac{1}{2}\epsilon_0|\nabla\phi_{\mathrm{el}}(\mathbf{r})|^2 + \epsilon_0\chi_{\mathrm{el}}(\mathbf{r})|\nabla\phi_{\mathrm{el}}(\mathbf{r})|^2 \right. \\ &\quad \left. + \epsilon_0\chi_{\mathrm{or}}(\mathbf{r})|\nabla\phi_{\mathrm{or}}(\mathbf{r})|^2 - \Gamma(\mathbf{r})u(\mathbf{r}) - \Gamma(\mathbf{r})\frac{1}{\beta v}\right\} \\ &= \int d\mathbf{r} \left\{\frac{1}{2}\epsilon_0|\nabla\phi_{\mathrm{el}}(\mathbf{r})|^2 + \epsilon_0\chi_{\mathrm{el}}(\mathbf{r})|\nabla\phi_{\mathrm{el}}(\mathbf{r})|^2 \right. \\ &\quad + \epsilon_0\chi_{\mathrm{or}}(\mathbf{r})|\nabla\phi_{\mathrm{or}}(\mathbf{r})|^2 - \frac{1}{\beta v}\Gamma(\mathbf{r}) \\ &\quad \left. - \frac{1}{\beta v}\Gamma(\mathbf{r})\log\left[\frac{\sinh\beta\bar{\mu}|\nabla\phi_{\mathrm{or}}(\mathbf{r})|}{\beta\bar{\mu}|\nabla\phi_{\mathrm{or}}(\mathbf{r})|} e^{\frac{\beta\alpha}{2}(\nabla\phi_{\mathrm{el}}(\mathbf{r}))^2}\right]\right\} \\ &= \int d\mathbf{r} \left\{\frac{1}{2}\epsilon_0(1+\chi_{\mathrm{el}}(\mathbf{r}))|\nabla\phi_{\mathrm{el}}(\mathbf{r})|^2 + \epsilon_0\chi_{\mathrm{or}}(\mathbf{r})|\nabla\phi_{\mathrm{or}}(\mathbf{r})|^2 \right. \\ &\quad \left. - \frac{1}{\beta v}\Gamma(\mathbf{r})\log\left[\frac{\sinh\beta\bar{\mu}|\nabla\phi_{\mathrm{or}}(\mathbf{r})|}{\beta\bar{\mu}|\nabla\phi_{\mathrm{or}}(\mathbf{r})|}\right] - \frac{1}{\beta v}\Gamma(\mathbf{r})\right\} \end{aligned} \tag{A9}$$

which is the expression for saddle-point free energy, Eq. (18). The last term in the integrand describes the translational entropy of the solvent molecules.[60]

APPENDIX B: TREATMENT OF THE SOLUTE CAVITY IN THE EVALUATION OF REORGANIZATION ENERGY

In this section, we present the general strategy for evaluating the reorganization energy and show that the divergent part in the saddle-point free energy G is canceled in the evaluation. In this work, the solute cavity is treated as part of the nuclear configuration parameter $\mathbb{C}$ to the saddle-point free energy. To allow for difference in solute cavities in the reactant and the product states, we reference each free energy to that of a state in vacuum with the same charge distribution, so that the free energy contribution from within the cavity is canceled. The resulting dependence of reorganization energy λ on the solute cavities $\Gamma^{\mathcal{R}}$ and $\Gamma^{\mathcal{P}}$ is explicitly included in Eq. (B4).

Let $G_0[\hat{\rho}_c]$ be the free energy of the charged distribution $\hat{\rho}_c(\mathbf{r})$ in vacuum. In a vacuum, $\chi_{\text{or}} = \chi_{\text{el}} = 0$, and the saddle-point free energy reduces to

$$G_0 = \int d\mathbf{r}\, \frac{1}{2}\epsilon_0 |\nabla\phi_0(\mathbf{r})|^2, \tag{B1}$$

where $\phi_0(\mathbf{r})$ is the electric potential in the vacuum calculated through Poisson equation (16a) or

$$\phi_0(\mathbf{r}) = \int d\mathbf{r}' \frac{\hat{\rho}_c(\mathbf{r})}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|}. \tag{B2}$$

Starting from Eq. (21), we subtract and add the free energy of vacuum charge distribution $\hat{\rho}_c^{(P)}$, i.e.,

$$\lambda = (G[\mathbb{C}^{\mathcal{R}}, \hat{\rho}_c^{(P)}] - G_0[\hat{\rho}_c^{(P)}]) - (G[\mathbb{C}^{\mathcal{P}}, \hat{\rho}_c^{(P)}] - G_0[\hat{\rho}_c^{(P)}]). \tag{B3}$$

In each of the brackets in the above equation, the contributions to the free energy from the region within the solute cavity cancel off, so the integral in each bracket only needs to be evaluated outside the solute cavity. Therefore, the reorganization energy can be calculated as

$$\begin{aligned}
\lambda = & \int d\mathbf{r}\, \Gamma^{\mathcal{R}}(\mathbf{r}) \left\{ \frac{1}{2}\epsilon_0(1+\chi_{\text{el}}^{\mathcal{N}}(\mathbf{r}))|\nabla\phi_{\text{el}}^{\mathcal{N}}(\mathbf{r})|^2 \right. \\
& + \epsilon_0\chi_{\text{or}}^{\mathcal{R}}(\mathbf{r})|\nabla\phi_{\text{or}}^{\mathcal{R}}(\mathbf{r})|^2 - \frac{1}{\beta v}\log\left[\frac{\sinh\beta\bar{\mu}|\nabla\phi_{\text{or}}^{\mathcal{R}}(\mathbf{r})|}{\beta\bar{\mu}|\nabla\phi_{\text{or}}^{\mathcal{R}}(\mathbf{r})|}\right] \\
& \left. - \frac{1}{2}\epsilon_0|\nabla\phi_0^{(P)}(\mathbf{r})|^2 \right\} \\
& - \int d\mathbf{r}\, \Gamma^{\mathcal{P}}(\mathbf{r}) \left\{ \frac{1}{2}\epsilon_0(1+\chi_{\text{el}}^{\mathcal{P}}(\mathbf{r}))|\nabla\phi_{\text{el}}^{\mathcal{P}}(\mathbf{r})|^2 \right. \\
& + \epsilon_0\chi_{\text{or}}^{\mathcal{P}}(\mathbf{r})|\nabla\phi_{\text{or}}^{\mathcal{P}}(\mathbf{r})|^2 - \frac{1}{\beta v}\log\left[\frac{\sinh\beta\bar{\mu}|\nabla\phi_{\text{or}}^{\mathcal{P}}(\mathbf{r})|}{\beta\bar{\mu}|\nabla\phi_{\text{or}}^{\mathcal{P}}(\mathbf{r})|}\right] \\
& \left. - \frac{1}{2}\epsilon_0|\nabla\phi_0^{(P)}(\mathbf{r})|^2 \right\} - \int d\mathbf{r}\, \frac{1}{\beta v}(\Gamma^{\mathcal{R}}(\mathbf{r}) - \Gamma^{\mathcal{P}}(\mathbf{r})),
\end{aligned} \tag{B4}$$

where the superscripts $\mathcal{R}$, $\mathcal{N}$, and $\mathcal{P}$ refer to the states (indicated in Fig. 1) at which the susceptibilities, potentials, and solute cavities are defined, and $\phi_0^{(P)}$ denotes the potential in a vacuum with the product charge distribution $\hat{\rho}_c^{(P)}$.

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